

Simulation of Positronium in Silica Sodalite

P. Hastings, A. L. R. Bug and P. A. Sterne

This article was submitted to The 13th International Zeolite
Conference, Montpellier, France, July 8-13, 2001

April 17, 2001

U.S. Department of Energy

Lawrence
Livermore
National
Laboratory

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This report has been reproduced directly from the best available copy.

Available electronically at <http://www.doc.gov/bridge>

Available for a processing fee to U.S. Department of Energy
And its contractors in paper from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-mail: reports@adonis.osti.gov

Available for the sale to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-mail: orders@ntis.fedworld.gov
Online ordering: <http://www.ntis.gov/ordering.htm>

OR

Lawrence Livermore National Laboratory
Technical Information Department's Digital Library
<http://www.llnl.gov/tid/Library.html>

SIMULATION OF POSITRONIUM IN SILICA SODALITE

Peter Hastings and Amy L.R. Bug (corresponding author)

Dept. of Physics and Astron., Swarthmore College, Swarthmore, PA 19081, USA

Philip Sterne Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

SUMMARY: We find the annihilation rate of positronium (Ps) within silica sodalite. Positron density and the electronic density seen by positrons are compared with a semi-empirical "free volume" model.

INTRODUCTION: Positron annihilation spectroscopy (PAS) is a versatile tool for the study of solid atomic and electronic structures. Defects and voids are characterized by the annihilation rates of injected positrons which migrate into void spaces. In the zeolite literature PAS studies have been used to (i) provide support, given known sizes of zeolite cages, for simple "free volume" (FV) theories of positron annihilation [1], (ii) predict anomalies in the zeolite structure [2], (iii) infer the locations of water and other adsorbates [3].

In insulating materials like zeolites, a positron thermalizes in a few tens of ps , and may strip an electron from the lattice to form positronium (Ps) [4]. An important decay signature in PAS/zeolite studies, with a typical lifetime, τ , of several ns , is the "pick-off" decay of ortho-Ps with another electron of the host lattice. (τ for free ortho-Ps is 140 ns .) The lifetime of ortho-Ps can be expressed as

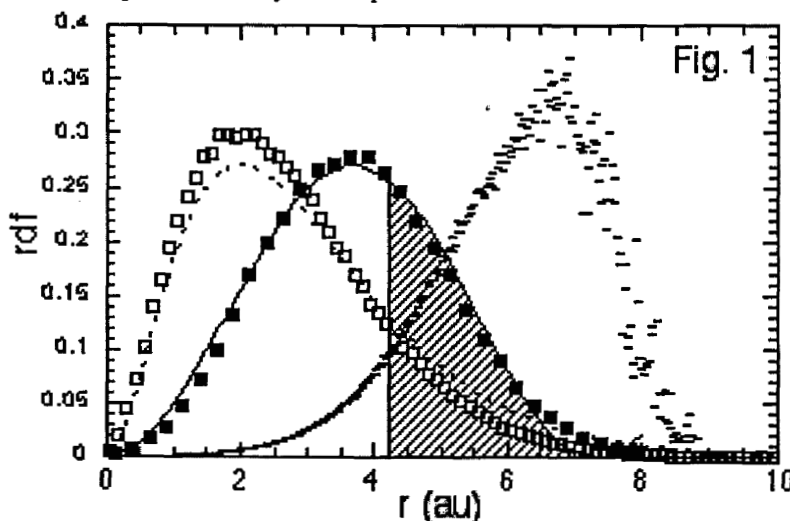
$$\tau^{-1} = \pi r_e^2 c \int dr_+ dr_- n_+(r_+) n_-(r_-) \gamma[n_-] \delta(r_+ - r_-) \quad (1)$$

where r_e is the classical electron radius, $n_{+,-}$ the density of positrons, electrons (respectively), and γ the "enhancement" which tends to unity as $n_- \rightarrow \infty$ and corrects for the fact that an electronic density represents a many-electron system.

A FV model allows one to obtain approximate agreement with experimental lifetimes in the α cages of zeolites A and X [5]. Still, it is clear that some of the assumptions of this model - spherical zeolite cages, confinement to cages only, uniform electronic density in a layer at the walls, Ps acting as a particle of mass $2m_e$ in a "box" - are not microscopically valid. Here we report on a detailed calculation of Eq. (1) for Ps in a zeotype. We consider silica sodalite, the silicon polymorph of sodalite: a close packed arrangement of sodalite cages.

METHODS: The solid is cubic (Im3m) with $a = 8.83\text{\AA}$ and unit cell $\text{Si}_{12}\text{O}_{24}$. While one expects charge transfer between neutral O and Si and further adjustment of charge due to the introduction of the Ps, for now we neglect these effects. An atom-based density functional code [6] calculates electronic density $n_i^l(r)$ at distance r from each atomic center i ; these are superposed to form $n_-(r)$. The two particles of Ps interact via a Yukawa approximation [7] to the Coulomb potential: $V(r) = -e^2/r$. The positron interacts with lattice ions via Coulombic repulsion, and with electronic density via a Hartree plus a correlation attraction [8]. The electronic pseudopotential is difficult to calculate; here it is modeled as a sum of exponentials [9]. The Ps orbital, hence $n_+(r)$, is sampled with Path Integral Monte Carlo (PIMC). For computational efficiency, host-Ps potentials are first calculated on a $40 \times 40 \times 40$ spatial grid, and cubic spline interpolation used to find the potential at location r . PIMC is a finite-temperature technique. Data were generated with $P = 1000$ electron and positron beads at $T = 0.02\text{ au}$. Lower temperature results are forthcoming.

RESULTS AND DISCUSSION: The open squares in Fig. 1 give the relative radial density function (rdf) of the Ps atom; the 1s orbital is shown as a dashed line. Closed squares give the rdf of positrons within the first unit cell of the crystal. This can be fit (though the data has an asymmetry which the fitting form cannot reproduce) to a "particle-in-a-box" rdf (solid curve) of the form $\sin^2(\pi r/R+\Delta R)$, giving $R+\Delta R = 7.3 \text{ au}$. (As T decreases this radius increases, as Ps becomes more delocalized.) In Ref. 10 $R+\Delta R = 9.4 \text{ au}$ was inferred from the experimental lifetime, $\tau = 2.5 \text{ ns}$, in aluminosilicate sodalites. The FV model predicts $\tau^{-1} = 2A \text{ ns}^{-1}$ [1], where the probability A corresponds to the hatched area in Fig. 1, within $\Delta R = 3.1 \text{ au}$ (1.66 \AA) of the cavity wall. Dashes in Fig. 1 show a normalized rdf of $n_-(r)$ ($n_+(r)$). This curve (see Eq. (1)) might be compared with the hatched region of the solid curve, where uniform charge density is assumed to produce annihilation in the FV model. When calculated from Eq. (1), τ depends quite sensitively on the model used for γ . For insulators, a constant enhancement is sometimes used; while for metals, enhancement decreases with $n_-(r)$ [11]. Taking the polarizability of the walls to be $\alpha = 26 \text{ au}$, for example, we derive $\gamma = 2.3$, predicting that $\tau = 5.5 \text{ ns}$ for the insulator model. For the metal model, $\tau = 2.0 \text{ ns}$. These bounds compare reasonably with experiment in aluminosilicate sodalites.



ACKNOWLEDGMENTS: Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society. Additional support was provided by the Faculty Research Support Fund of Swarthmore College. We thank L. Larrimore, R. MacFarland, G. Galli and F. Gygi. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng.48.

REFERENCES: [1] Y.C. Jean in *Positron Spectroscopy of Solids*, A. Dupasquier and A.P. Mills Jr., Eds. (IOS press, Amsterdam, 1995), p.563. [2] H. Nakanishi and Y. Ujihira, *J. Phys. Chem.* **86**, 4446 (1982). [3] M.B. Perkal and W.B. Walters, *J. Chem. Phys.* **53**, 196 (1970); A.M. Habrowska and E.S. Popiel, *J. Appl. Phys.* **62**, 2419 (1987). [4] T. Hyodo in Ref. [1], p. 419. [5] K. Ito, H. Nakanishi and Y. Ujihira, *J. Phys. Chem. B* **103**, 4555 (1999). [6] P.A. Sterne and J.H. Kaiser, *Phys. Rev. B* **43**, 13892 (1991) [7] L. Larrimore, R. M. McFarland, P. Sterne and A.L.R. Bug, *J. Chem. Phys.* **113**, 10642 (2000). [8] M. Kimura, O. Sueoka, A. Hamada and Y. Itikawa, *Adv. Chem. Phys.* **111**, 537 (2000); [9] B. Space, D.F. Coker, Z.H. Liu, B.J. Berne and G. Martyna, *J. Chem. Phys.* **97**, 2002 (1992) [10] A. Baranowski, M. Debowska, K. Jerie, A. Jezierski and M. Sachanbinski, *Acta Physica Polonica A* **88**, 29 (1995); [11] M.J. Puska, S. Mäkinen, M. Manninen and R.M. Nieminen, *Phys. Rev. B* **39**, 7666 (1989).